RIDER GROUP STANDARD OPERATING PROCEDURES
(revised 2017-05-03)

ROTARY EVAPORATOR

1. Process

Evaporation of solvent under normal or reduced pressure. The equipment consists of the rotary evaporator, and a heated water bath.

2. Hazardous Chemicals

a) Solvents (acetonitrile, benzene, toluene, hexane, ethanol, ether, THF, chloroform, methylene chloride, etc.). Some of these are flammable and some are carcinogenic.

3. Personal Protective Equipment

Goggles must be used, especially with reduced pressure evaporation.

4. Engineering/Ventilation Controls

Relocating the equipment to a fume hood is required for the distillation of carcinogenic solvents, toxic solvents or pyridine. See lab supervisor for assistance if no other option is available.

5. Handling Procedures

Equipment

Ensure that cooling water is turned on and that pressure relieve valve on top of condenser is open. Charge evaporator flask with solution (in fume hood) and connect to condenser while motor is in elevated position. Secure flask with keck clip and turn on motor on slowest setting. Adjust rotating speed, and immerse flask in water bath using the lift. Do not apply vacuum when low boiling solvents (Bp <60 deg Celcius) are evaporated, because these solvents will not condense under reduced pressure. When finished, first open pressure relieve valve (after work under reduced pressure), lift flask out of water bath, reduce rotational speed and turn of motor, then disconnect flask with residue. Dispose organic solvent distillate in appropriate waste container. Turn off water. Clean spills into the condenser. Clean condenser, when water or carcinogenic solvents have been evaporated.

Some Boiling points of common organic solvents.

Solvent	b.p. °C	suggested controller setting	appropriate gloves[c]	inappropriate gloves
Benzene[b]	80	5	SS best, V ok	B, N, R
Diethyl ether[a]	34.5	4	SS	V, B, N, R
Hexane	69	5	SS, V, N	B, R
Methanol	65	5	N, R	
Methylene chloride	40	4.5	SS best, V ok	B, N, R
Pentane	36	4.5	SS, V, N	B, R
Pyridine[b]	116	6	SS	B, N, R
Tetrahydrofuran	67	5	SS	V, B, N, R
Toluene	111	6	SS, V	B, N, R

[a] Boiling point is so low that vapours may travel through condensers and contaminate lines and other stills. [b] Need to be distilled in a fume hood.
[c] SS=Silver Shield, V=Viton, B=Butyl, N=Nitrile Latex, R=natural rubber

6. Accident Procedures

- Fire fighting efforts should only be attempted for small fires. A fully loaded evaporator flask could rapidly become too large a fire. In such a case, evacuate the lab, close the door, and call WWU's emergency line, or pull the fire alarm. Any fire fighting efforts, by laboratory staff or fire fighting personnel should be aimed at putting out the solvent fire.
- If there is a significant spill of flammable material, keep all spark sources away. Keep lab doors and windows closed; the fumehood will exhaust the room and keep it at negative pressure with respect to the hall and other rooms. Call WWU's emergency line to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.
- Cleanup of the mess after an accident should be performed carefully.

7. Decontamination

See waste disposal

8. Preventive measures

- Never leave the apparatus unattended while in operation.

9. Maintenance:

- Check whether the seals are in reasonable condition and tight. Check for squeaking noises. If necessary, disassemble glassware and clean it.

INERT ATMOSPHERE GLOVE BOX

- Use of the glove box is restricted to those researchers who have been trained in its use by the PI or by an experienced user and with the approval of the PI.
- For first hand information consult the VAC Atmospheres reference manual.

0. General remarks

- **Never** attempt to wash the plexiglass windows with organic solvents. The windows will fog as a result of partial dissolution of the plexiglass, and all users will have to watch future experiments through a haze. Instead, clean the windows from inside with a **dry Kimwipe**, and from the outside with water with some dishwashing agent.

- **Never** open both antechamber doors simultaneously. Air will leak in, and your and your colleagues' chemicals will decompose.

- **Never** rush out of the gloves so quickly, that sub-atmospheric pressure is applied to the glove box. Air will come in through microscopic leaks, with mentioned consequences.

- **Never** open the inner door of the antechamber when you are not absolutely sure that the antechamber is under a clean nitrogen atmosphere. If you have doubt about the state of the antechamber, apply three evacuation/nitrogen purge cycles. When not in use, keep the antechambers under vacuum.

- **Never** release any chemicals into the glove box atmosphere. Most chemicals react with the catalyst and significantly reduce its lifetime. More importantly, vapors of harmful solvents/chemicals can penetrate the butyl rubber gloves and damage your health. Keep in mind, that the glove box is a closed system, and that everything you release into the atmosphere may at some later point interfere with either you or your experiments. Accordingly, do not carry out strongly exothermic reactions in the box, which may result in chemical spills. Because we cannot use reflux condenser in the box, never heat any chemical near its boiling point in the box ($T < T_{b.p.} - 20°C$).

1. Process

The glove box is used for storage or handling of air/moisture sensitive chemicals (i.e. chemicals which are either dangerous or rendered useless when exposed to air or water). The glove box is further used for carrying out small scale (<20 mL solvent) reactions that involve air and moisture sensitive compounds. Exceptions from this rule require the permission of the PI.

2. Hazardous Chemicals

All chemicals are to be stored in closed vessels within the glove box and this is especially important for hazardous and pyrophoric chemicals. Most chemicals react with the catalyst and significantly reduce its lifetime. More importantly, vapors of harmful solvents/chemicals can penetrate the butyl rubber gloves and damage your health. Keep in mind, that the glove box is a closed system, and that everything you release into the atmosphere may at some later point interferes with either you or your experiments.

Other hazards of the glove box include overpressurization and venting of noxious materials. The gas purification catalyst consists of metals and their oxides which may react violently with air or water. The operating gas is nitrogen and the regeneration gas is a few percent hydrogen in argon. These gases are not toxic but will not support life.

3. Personal Protective Equipment

Operators should wear fresh nitrile or reusable cotton gloves on their hands and put baby powder on the gloves if perspiration has occurred. These precautions help prevent the buildup of sweat, which renders the skin more permeable to chemicals. If carcinogens such as chloroform or benzene are handled inside the glove box, wear a pair of Silver Shield or Viton gloves inside the box and over the main gloves. The main gloves themselves are either butyl rubber or neoprene and therefore will not protect you from such chemicals.

4. Handling Procedures

Refer to the glove box reference manual for proper operating procedure.

Some general advice:

• After the antechamber has been evacuated for 25 min and filled with nitrogen, write IN on the dry erase board on the chamber.

• If you open the outside door to the antechamber, change the note on the dry erase board to OUT.

• If you take things out, change the sign to OUT.

• If the antechamber hasn't been used for a few days, change the note on the dry erase board to OUT.

• Never open both doors to an antechamber at the same time.

• Always take all visible rubbish out with you even if it is not your rubbish.

• Put rubbish into the dustbin inside the box. Dispose of sharps outside of the glove box immediately after use.

• If you break glass, pick up all the pieces (with tweezers, not gloves) right away.

• Keep flasks covered/closed if they contain liquids.

• The following chemicals are not permitted inside the glove box: H_2, H_2O, CO, air, O_2, N_2O, HF, HCl, HBr, HI, HCN, HCO_2H, NH_3.

• Avoid using chromatography columns in the box unless absolutely necessary. The silica/alumina powders plug up the oxygen monitor. Clean up powders as soon as possible, avoiding dispersing them in the box.

***What kind of objects can be brought through the antechambers into the glove box*:**

- Ensure that evacuated flasks are secured against falling.
- If possible, objects should be dried over several hours in the drying oven prior to introduction into the antechamber.

a) Solid objects such as glassware, metal implements, open boxes of Kimwipes, etc. may be brought in as long as they are not capable of trapping air.

b) Reagents which are in their original unopened bottles and were packaged under argon may be brought into the glove box without further preparation. The unopened bottle is all the containment that is required.

c) Dried and distilled solvents from the stills must be transferred into a solvent flask which has been evacuated to a minimum possible pressure which depends on the solvent. Stopcocks have to be secured with clamps, and rubber bands, and must be at room temperature. Flasks must be contained in secondary containers.

d) Other liquids should be degassed. The liquids should be at room temperature when they go through the antechamber.
e) Bottles or jars of air-stable solids should be opened, and a folded Kimwipe should be placed over the jar and held down with rubber bands to protect powders from spilling out into antechamber and vacuum pump. The original cap should go into the glove box along with the Kimwipe-covered jar.

Bringing an object into the glove box via the large antechamber.
Ensure that inside door, vacuum valve and the N_2 refill valve are closed, and that the antechamber pressure is ~1 atm. Further ensure, that the vacuum valve of the big antechamber is closed (If the antechamber pressure is at a very low value refill the antechamber with N_2 from the glovebox space with the refill valve). Open the outside door, place object inside the antechamber, close the outside door, and slowly open vacuum valve while listening to the interior of the chamber. Evacuate antechamber until vacuum is attained for at least for 25 minutes. Close vacuum valve, open refill valve slowly until the interior pressure reaches an atmospheric level, close refill valve. Open inside door, extract object, close inside door. Change dry erase board to "IN". For long periods (standby), leave antechamber under vacuum.

Procedure for bringing an object out of the glove box.
Ensure that the outside door is closed and the dry erase board says "IN" (if the dry erase board says "OUT" then you have to go through the "bringing in" procedure as described above, before trying to bring anything out). Open the inside door, place object inside the antechamber. Close the inside door. Open outside door, extract object, close outside door. Change dry erase board to "OUT".

5. Accident Procedures

If for some reason the pressure climbs too high so that the gloves start to balloon, close the main valve on the cylinder supplying the inert gas. If the gloves burst, close the main valve on the cylinder supplying the inert gas and put the port cover in place to block off the burst glove. This will prevent the smell of the glove box from spreading into the room and will also minimize the contamination of the glove box with air.

In case of a fire or overheating of the drying catalyst during regeneration, close the main valve on the cylinder which is supplying the regeneration gas (H_2/Argon) to the glove box.

If inert gas has been or is being released and there is no danger of fire, close the valve to the inert gas supply.

If a glove breaks, rips or is punctured, use that hand to pull the glove port cover over the glove hole. The glove port cover should be stored near the back of the glove box. Read the operating manual to find out how to replace the damaged glove. (Note: during the procedure for flushing the new glove, do not evacuate the new glove so much that the knob on the glove port cover becomes too difficult to turn.)

Power Outage.
If the oxygen level rises above 1000 ppm, stop the recirculation, solve the leak, then purge with N_2 or argon until the O_2 level falls to 200 ppm and then start the recirculation again until the level falls to below 10 ppm. If the oxygen level rises slowly or fails to

come down after a leak despite continued recirculation, regenerate the catalyst as described in the manual.
If the oxygen level is high and does not respond to purging with fresh N_2, or if the measured oxygen level does not seem to correspond to the true oxygen level, then the circulation may be turned off.
The true oxygen level can be checked independently by the following procure: a) remove the upper half of the glass from a normal 60 watt light bulb using a glassblowing torch, b) bring this light bulb into the glove box, c) put it into a lamp socket clamp onto a stand, and d) turning on the lamp. If the light bulb glows for more than a minute, then the oxygen level is very low (probably less than 10 ppm).

6. Waste Disposal

Chemical waste has to be removed from the glove box in suitable containers, e.g. sealed plastic bags for used kimwipes, or flasks for both liquid and solid chemicals. The latter have to treated according to waste disposal regulations. Used pump oil should be put into a properly labeled hazardous waste container.

7. Decontamination

All materials exposed to hazardous chemicals in the glove box have to be decontaminated in a fume hood.

8. Preventive measures

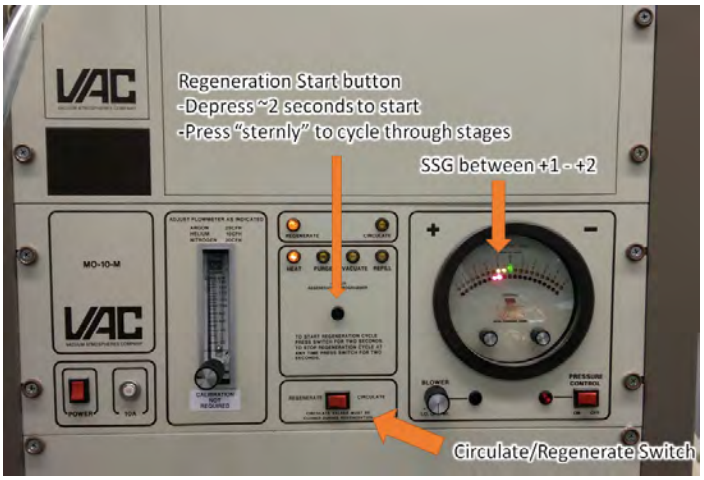
- The following materials are banned from being introduced into the glove box: mercury, air, oxygen, nitrogen oxides, sulfur oxides, sulfuric acid, nitric acid, hydrochloric acid, aqueous solutions, water, halogens, and any other chemicals related to any of the above. Alcohols may be introduced but preferably in only small quantities and only used with a closed circulator and subsequent atmosphere purge.

9. Maintenance:

- Every 2 months, check that the oil in the vacuum pump is clear and nearly colorless and of sufficient volume (as indicated by the markings on the view window).
- Every 2 months, clean the condenser fins on the Dri-Cold refrigerator. Check the sight glass, located in the condensing line, for presence of moisture (refer to manual if moisture is detected). Replace battery if the display is dim (refer to manual).
- Every 2 months, visually check the gloves and the O-rings around them for punctures, cracking, or wear; replace the gloves or o-rings if cracks are found. Check the O-rings on the antechamber doors for cracks; replace the o-rings if cracks are found. Clean the doors with a mild solvent and coat the sealing surfaces with a light coat of vacuum grease (Apiezon, not silicone).
- Every 6 months, replace the oil in the vacuum pump.
- Every year, perform maintenance on the vacuum pump as called for in its manual.

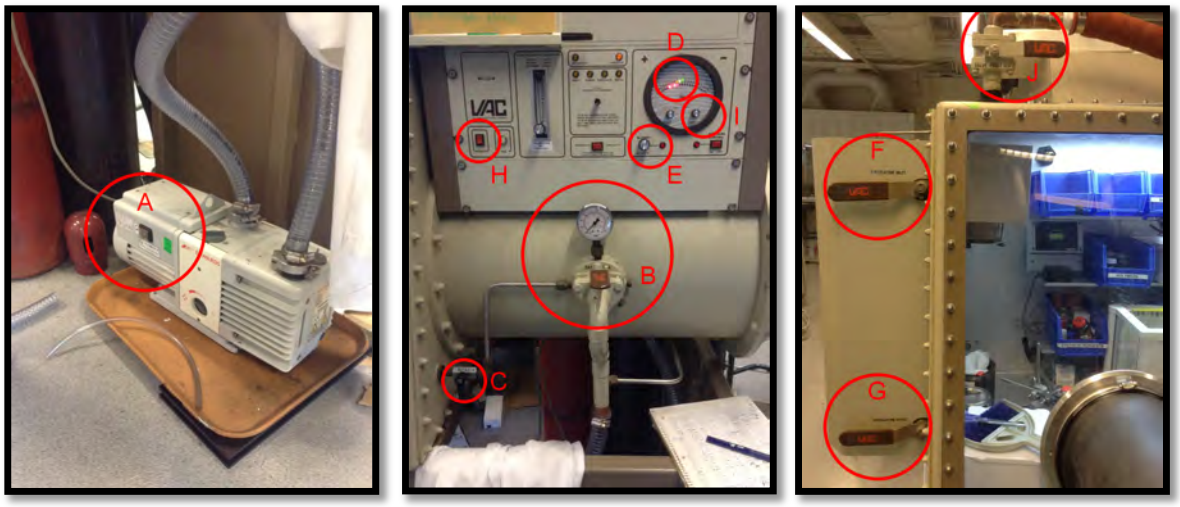
10. Glovebox Catalyst Regeneration (MO-10-M from VAC)

Updated 11/19/2014 Satu Heiskanen and Erik Benton



1) Adjust SSG pressure gauge as to have 3 red lights between +1 to +2 (left side of gauge)
2) Turn off blower, close catalyst circulation valves (vert. is closed)
3) Attach hydrogen rated regulator to a full tank of Nitrogen/Hydrogen (92.5/7.5) mix gas. Check for leaks.
4) Set regulator to 10 PSI, open needle valve part way.
5) Turn switch from "circulate" to "regenerate"
6) Press regeneration start button for 2 seconds, regenerate light will turn on
   a. Depress "sternly", release, the "heat" light should be illuminated
   b. Depress "sternly", release, the "purge" light should be illuminated
   c. The bearing in the flow rate controlled is expected to spike upwards, and then stabilize at a lower value
   d. Adjust flow rate to between 20 and 40 CFH using both the flow rate controller and the needle valve
   e. Depress the regeneration start button until the regeneration light turns off. This means the system is no longer running the regeneration program.
   f. Repeat steps a-e allowing the gas to flow for 1 minute to ensure that the flow rate is set to the desired value.
7) To start the regeneration program depress the regeneration start button for 2 seconds, and wait approximately 3 minutes for the heating light to automatically turn on.
8) Check on regeneration progress approximately 3.5 hours into the total 12 hour time. Check for the following:
   a. Water condensed in the trap, located behind the antechamber
   b. Gas flow rate controller shows the desired flow rate
9) After the regeneration is complete:
   a. Empty the trap of water
   b. Return switch to "circulate" mode.
   c. Manually purge glovebox
   d. Restart the blower fan by dialing up the blower knob until you hear the motor begin to run. You may have to place your ear against the glovebox window to hear it. Initially, you'll hear a groaning and then a nice medium/high pitch as you get it running at an appropriate speed.
   e. Open circulation valves

11. **Short Term** (~1-2 days) **Shut-down Procedure**



1) Turn off all interior electronics: stir/hot plates, overhead light (switch in middle up top) etc. Leave the O_2 sensor and balance on and plugged in. Unplug the glove box electrical line to these devices (follow the line at back). Note the O_2 level.

2) Fill the vacuum line and access port with N_2.
   a. Turn off the vacuum pump with the switch on the unit (**A**).
   b. Open the vacuum valve, (**B**) (parallel to thick piping).
   c. Bleed open the refill valve (**C**)(~ 45° to line) to fill the vacuum line and port with N_2 from the main glove box area.
   d. When complete, close vacuum valve (**B**) and the refill valve (**C**) (perpendicular to thick piping).

3) Make note of the initial pressure settings.
   a. In the +/- panel at right (**D**). Generally, the top arch of lights will be illuminated from 0 to half way along the illuminated portion of the arch below. The illuminated arch below will be illuminated from 0 to 3" of water.
   b. Notice the illuminated Pressure Control Light is on.
   c. Notice the illuminated Circulate Light is on.
   d. Notice the illuminated Blower Light is on.
   e. Notice the illuminated Regenerate/Circulate switch is depressed to "Circulate".

4) Make note of the initial blower position (~ pointing directly at "L). Dial the blower knob (**E**) down (counterclockwise) to "off." Make note of where this was initially.

5) Close both catalyst valves (**F** and **G**) (perpendicular to thick piping).

6) Depress the main power (**H**) button to the down position.

7) Inspect for errors, additional electronics requiring powering down.

8) Fill out glove box logbook with activity, O_2 level and date.

9) AFTER SHUT DOWN ACTIVITY IS COMPLETE PROCEED TO NEXT STEP

10) Depress the main power (**H**) button to the up position. Wait for system pressure to equilibrate. Compare to initial pressure settings.

11) Check the main N_2 tank for sufficient N_2 (minimum 1000 psi required). Install new tank if needed.

12) Purge the glove box.
   a. Temporarily increase the operating pressure range with the **I** knob such that the bottom illuminated arch on the +/- panel (**D**) is illuminated from 0/1 to 5" of water. Wait for the system pressure to equilibrate.
   b. Bleed open the purge vent valve (**J**)(~ 45° to line) until venting occurs. You should notice a clicking sound every 1-2 seconds for the solenoid valve at the main N_2 tank. Purge ~ 500 psi through the system by watching the pressure reading at the main N_2 tank.
   c. When purge complete, close the purge vent valve (**J**).
   d. Decrease the operating pressure range with the **I** knob such that the bottom illuminated arch on the +/- panel (**D**) is illuminated from 0-3" of water. Wait for the system pressure to equilibrate.

13) Open both catalyst valves (**F** and **G**).

14) Slowly dial up the blower knob (**E**) until you hear the motor begin to run. You may have to place your ear against the glovebox window to hear it. Initially, you'll hear a groaning and then a nice medium/high pitch as you get it running at an appropriate speed. It should be set to a setting similar to where it was initially (~ pointing directly at "L).

15) Turn the pump back on by using switch (**A**).

16) Open the vacuum valve, (**B**) (parallel to thick piping) to fully evacuate the chamber. Ensure that the refill valve (**C**) is closed at this point.

17) Inspect for errors.

18) Replace the glove box electrical line to provide power to the internal devices (follow the line at back). Turn on the overhead light (switch in middle up top). Note the O_2 level.

19) Fill out glove box logbook with activity, O_2 level and date.

GLOVE BOX ATMOSHERE CHECK

Oxidation of titanocene complex by O_2

Use of a Titanium Metallocene as a Colorimetric Indicator for Learning Inert Atmosphere Techniques

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We have recently discovered that titanium(III) metallocene compounds provide a very useful visual aid for students learning standard Schlenk vacuum line techniques (*1*). Our process for training students in these procedures begins by demonstrating various anaerobic techniques such as solvent degassing, solution transfer through a cannula, and filtering through frits or immersion filters (*2*). The students are then instructed to practice these techniques using a solution of a Ti^{3+} metallocene (preparation described below). A striking blue to yellow color change provides an immediate signal that helps students to judge whether they performed an operation correctly. This experience accelerates the learning process and rapidly increases their self-confidence to work independently on the vacuum line. Both undergraduate and graduate students new to the research lab have benefited from this exercise and have gained respect for the care needed to successfully accomplish operations with rigorous exclusion of dioxygen gas.

A solution of the reactive Ti(III) metallocene indicator can be easily prepared in situ in a Schlenk flask attached to a Schlenk vacuum line. Dicyclopentadienyltitanium(IV) dichloride (cyclopentadienyl, C_5H_5, hereafter referred to as *Cp*; available from Aldrich Chemical Co. as *titanocene dichloride*, catalog #23,482-6) is dissolved in deaerated acetonitrile followed by addition of zinc dust.[1] A slow reduction reaction[2] can be followed visually through a series of color changes. The initially orange-red solution of $TiCp_2Cl_2$ turns green as the dimer $(TiCp_2)_2(\mu\text{-}Cl)_2$ is formed (Fig. 1).[3] The appearance of a deep blue solution signals the formation of $[TiCp_2(NCCH_3)_2]^+$, a result of facile dimer cleavage in the coordinating solvent acetonitrile (*3*). When this is exposed to O_2, the deep blue color of $[TiCp_2(NCCH_3)_2]^+$ is rapidly bleached to yellow as Ti^{3+} is oxidized back to Ti^{4+}.

After preparation of the blue $[TiCp_2(NCCH_3)_2]^+$ solution in Schlenkware, students practice a variety of operations in which the reactive blue $[TiCp_2(NCCH_3)_2]^+$ solution will quickly indicate errors of technique. One common operation is the anaerobic transfer of solutions from one flask to another through a steel tube or cannula. Neglecting to purge the cannula of air by passing through inert atmosphere for several minutes or insufficient purging of the receiving flask by repetitive evacuation and N_2-refill cycles will be exposed to the student when the blue solution turns yellow during the transfer operation. As a second example, this colorimetric method helps students judge the nitrogen gas flow needed to permit the successful exchange of a rubber septum for a reflux column, glass stopper, or another piece of apparatus when the flask is opened.

We have also used the solution of $[TiCp_2(NCCH_3)_2]^+$ as a colorimetric indicator for oxygen contamination in inert-atmosphere glove boxes. Small quantities of the blue solution are conveniently prepared by dissolving small (mg) amounts of $TiCp_2Cl_2$ in acetonitrile in a scintillation vial, adding zinc dust, and capping. Aliquots of this solution may be removed by disposable piper and transferred to an open vial. Inspection of the aliquot gives a qualitative indication of the dioxygen level in the glove box. As the solution is exposed to trace dioxygen the solution color changes from blue to green and ultimately, under higher dioxygen concentrations, to yellow.

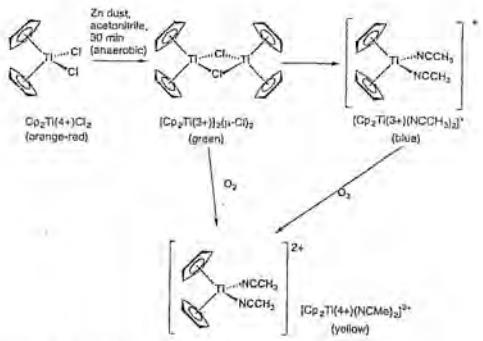


Figure 1. Reaction scheme for synthesis of the colorimetric indicator $[TiCp_2(NCCH_3)_2]^+$ and its reaction with dioxygen.

Acknowledgment

We thank John Bercaw for helpful comments regarding the bis(cyclopentadienyl)titanium chemistry.

Notes

1. Example quantities are 8 mg $TiCp_2Cl_2$ in 20 mL acetonitrile to which is added 6 g of zinc dust.
2. The reduction typically requires at least 15 min and is complete within 30 min.
3. If the reduction is carried out in tetrahydrofuran (THF) solution the reaction stops after formation of green $[TiCp_2]_2(\mu\text{-}Cl)_2$ and no blue species appears even after prolonged reaction times.

Literature Cited

1. Previous contributions to this *Journal* on the handling or preparation of air-sensitive compounds are Bohac, A. *J. Chem. Educ.* 1995, *72*, 263. Newton, T. *J. Chem. Educ.* 1991, *68*, A60. Newton, T. *J. Chem. Educ.* 1990, *67*, A232. Young, C. G.; *J. Chem. Educ.* 1988, *65*, 918–919. Walker, C. W.; Wade, W. L. *J. Chem. Educ.* 1987, *64*, 278. Villemin, D. *J. Chem. Educ.* 1987, *64*, 183. Lucas, C. R.; Walsh, K. A. *J. Chem. Educ.* 1987, *64*, 265–266.
2. An excellent text describing modern methods and equipment used in anaerobic work is *Experimental Organometallic Chemistry*. Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, D C, 1987.
3. Coutts, R. S. P.; Kautzner, B.; Wailes, P. C. *Aust. J. Chem.* 1969, *22*, 1137–1141.

Use of a Titanocene Complex as a Colorimetic Indicator for Learning Inert Atmosphere Techniques

Before beginning a full-scale preparation, you must first conduct the following simple test to determine your synthetic skills in handling air-sensitive compounds. This simple experiment will give you a quick and easy indication of whether you can manipulate an oxygen-sensitive compound through a variety of steps such as filtration, cannula transfer, and short-term storage. Note that the compound you're making is not water sensitive.

Procedure

Stir 0.1 g of Cp_2TiCl_2 in 20 mL of acetonitrile in a 100 mL Schlenk flask using a magentic stirrer. Bubble nitrogen through the solution via a cannula inserted through a Suba Seal inserted in the 24/40 joint (you'll also need to insert a vent).
Under a nitrogen counterflow, add a few grams of Zn *dust* and continue stirring. Periodically stop the stirrer and examine the solution.
When you have a nice blue/purple solution on settling, filter this into a Schlenk tube using a cannula with a Whatman #1 filter paper wired to it.
Practice manipulating the resulting solution:

- Put a few drops in a test tube in air to see how quickly it changes color (decomposes!).
- Use a syringe to see how well you can transfer the solution without decomposition
- Add some non-degassed acetonitrile to see the effect of dissolved oxygen.
- Stopper some of the solution to see how long your sample survives – compare with your neigbors.

When you can routinely handle these solutions, you're ready to move on to the experiments in the rest of Group A.

0.1 g Cp_2TiCl_2 in 20 mL CH_3CN = 0.02M

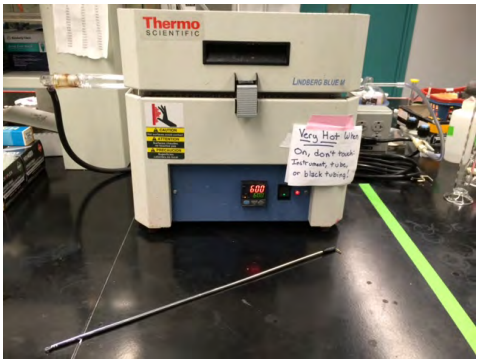
First, the box was purged with argon for one hour. A dark blue solution of [Cp2TiClCl]ZnCl2*2THF was then prepared and syringed onto a glass plate within the dry-box. After 10 min, during evaporation of the THF, the solution became olive green, indicating >5 ppm of oxygen. After 20 min the solution became deep orange, indicating a >20 ppm oxygen content. Since the moisture test indicated the absence of water for more than three days whereas the oxygen test indicated the presence of oxygen within 20 min, the gloves must be semipermeable to oxygen but impermeable to water. Therefore, an improvement in this box would be to incorporate neoprene or equivalent dry-box gloves. These range in price from $100 to $200.

For the Rider group glovebox:

1. Ready a dry 20 ml capacity vial with an inert threaded cap and stirbar.
2. Weight ~25 mg of titanocene dichloride ($Ti^{IV}Cp_2Cl_2$) into the 20 ml capacity vial.
3. Add ~15-17 mL of dry THF to this vial.
4. Add ~0.25 g of zinc dust to this vial (the smaller the grains of zinc the faster the reaction).
5. Stir the suspension for ~ 1-2 hrs [typically the reduction reaction which will transform the orange/brown $Ti^{IV}Cp_2Cl_2$ into a deep green/blue $Ti^{III}Cp_2Cl$ (titanocene monochloride) will take 30 min].
6. Once the reduction reaction is complete, stop stirring and allow the solution to settle.
7. Use a pipette to transfer the soluble portion to an eyedropper vial with a separate cap (primarily leaving behind zinc dust). Ideally, the vial is capped with an inert solid cap and the rubber bulb eyedropper type cap is only used when needed. The THF solvent will permeate through the rubber bulb if this is used as the long-term cap for the vial.
8. Store the full eyedropper vial in a secondary container to minimize the evaporation of the solvent.
9. The zinc dust and remaining suspension can be combined with any rinsing solutions used to clean previous vials. This solution can come out of the glove box without issue (a rapid color change is normal as the O_2 from air will rapidly oxidize the titanocene monochloride). Do not combine this waste with other general waste until the zinc is fully quenched. In a fume hood, carefully quench the zinc and titanocene monochloride waste with 100 mL of 0.1M hydrochloric acid.

LINDBERG MINI TUBE FURNACE

Updated 2017-05-03, Dr. Rider



General Safety

a) The tube furnace runs at extreme temperatures (up to 1000°C). Always make sure that the workspace near the tube furnace is ***free of flammable liquids and solids***!

b) Always make sure that sufficient purge gas is installed on the equipment.

c) Never touch parts of the tube furnace with bare hands.

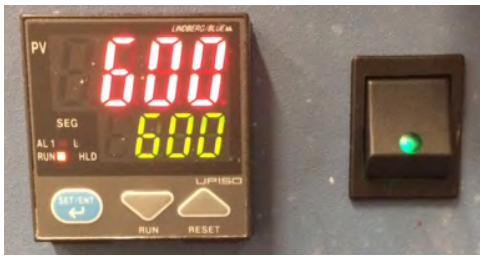
d) Make sure that all parts of the tube furnace are sufficiently cool before handling (including purge tubing).

e) Never touch the insulation on the inside of the tuber furnace. Never inhale particles from the insulation.

f) Do not touch or move the tube furnace housing while it is hot.

-- Standard Operating Procedure --

1) Fill in the logbook with the necessary information. If the purge gas tank is less than 200 psi, replace the tank or ask for assistance. (The required PSI in the tank is also dependent on your target runtime)
2) Remove all flammable solvents and materials from a 6 ft. perimeter around the tube furnace.
3) Place a sign near the tube furnace indicating that the unit is on and very hot. Email the research group to inform them on your runtime for the tube furnace.
4) Turn the main power switch on the front of the Lindberg Blue furnace to the on position. A green light in the button will illuminate. The red light to the right of it will stay dark.
5) Two numbers will appear on the UP150 control panel. The Red number indicates the chamber temperature, the green number indicates the instantaneous target set point.



The following instructions allow the user to program a tube furnace anneal consisting of: (i) a <u>15 min heat ramp</u> segment to a <u>temperature of 600°C</u> and (ii) a <u>hold at temperature of 600°C</u> segment that lasts <u>2.5 hours</u>. You may need to modify these instructions to fit your intended anneal program.

6) Press and hold the "Set/Ent" button. Two "node and rES" symbols will appear on the panel.
7) Press the "Set/Ent" button. Two "PrG and 0" symbols will appear on the panel.

8) Press the upward pointing triangle ∧ until a "1" appears on the panel instead of the "0." Press the "Set/Ent" button. Two symbols will appear: "SSP" and a green temperature value.
9) Press the upward and downward pointing triangles ∧, ∨ to adjust this temperature value to 20 (this is the starting temperature value). Press the "Set/Ent" button. Two symbols will appear: "StC" and a green number.
10) Keep the green value at 1. Press the "Set/Ent" button. Two symbols will appear: "SP1" and a green temperature value.
11) Press the upward and downward pointing triangles ∧, ∨ to adjust this temperature value to 600 (this is the final temperature of the ramp, or the first target setpoint value). Press the "Set/Ent" button. Two symbols will appear: "tn1" and a green number with the format of # . # # . The first number is the number of hours. The decimal number is the number of minutes (up to 60).
12) Press the upward and downward pointing triangles ∧, ∨ to adjust this number to indicate the ramp time of 0. 1 5 for the first segment. Press the "Set/Ent" button. Two symbols will appear: "SP2" and a green temperature value.
13) Press the upward and downward pointing triangles ∧, ∨ to adjust this number to match the temperature value at the end of the ramp. That is, 600. Press the "Set/Ent" button. Two symbols will appear: "tn2" and a green number with the format of # . # # .
14) Press the upward and downward pointing triangles ∧, ∨ to adjust this time value to the desired hold time, in this case 2.30. Press the "Set/Ent" button. Two symbols will appear: "SP3" and a green temperature value.
15) Press the upward and downward pointing triangles ∧, ∨ to adjust this number to match the temperature value at the end of the ramp. Press the "Set/Ent" button. Two symbols will appear: "tn3" and a green number with the format of # . # # .
16) If needed, press the upward and downward pointing triangles ∧, ∨ to adjust this time value towards 0. The temperature display will change to "oFF." Keep the value as "oFF."
17) Press the "Set/Ent" button. Two symbols will appear: "EU1" and a green value.
18) Keep the green value at 0. Press the "Set/Ent" button. Two symbols will appear: "AL1" and a green value.
19) Keep the green value at 9. Press the "Set/Ent" button. Two symbols will appear: "A1" and a green alarm value.
20) Press the upward and downward pointing triangles ∧, ∨ to adjust this alarm temperature value to be at least 50°C higher than any temperature in your program and usually less than 900°C. That is, 650 in this case. Press the "Set/Ent" button. Two symbols will appear: "Hy1" and a green value.
21) Keep the green value at 1. Press the "Set/Ent" button. Two symbols will appear: "EU2" and a green value.

22) Keep the green value at 0. Press the "Set/Ent" button. Two symbols will appear: "AL2" and a green word "oFF".
23) Keep green word as "oFF". Press the "Set/Ent" button. Two symbols will appear: "JC" and a green value.
24) Keep the green value at 0. Press the "Set/Ent" button. Two symbols will appear: "utE" and a green word "oFF".
25) Keep green word as "oFF". Press the "Set/Ent" button. Two symbols will appear: "SSP" and a green temperature value that should be identical to that from an earlier step (in this case 600). You have now cycled through all the options of the program
26) Press and hold the "Set/Ent" button to exit the programming portion of the exercise.

The following instructions allow the user to load glass samples into the tube furnace and purge the chamber with inert gas for 30 min.

27) Handle all parts of the tube furnace and fittings with **clean, grease and powder free gloves**. Contamination of the quartz tube will lead to concentrated defects in the quartz glass and will cause thermal stress in the quartz glass and ultimately a fracture of the tube.
28) Very carefully remove any wire (or other inflammable equivalent) that might be present to keep the glass tubing adapter in the female end of the quartz tube (see photo). Take care not to bend or force the expensive quartz tube.
29) Carefully twist the glass tubing adapter to remove it from the expensive quartz tube.
30) Carefully place the glass tubing adapter on a clean kimwipe in a dust-free and secure area. Note that the tension on the black tubing will want to move the adapter after you release it.
31) Use tweezers to carefully place a glass (or ITO or Si) substrate into the quartz tube. **Take care to avoid dragging the sample over the greased joint surface**.
32) Use a telescoping wand (see photo) to slide the sample towards the middle of the quartz tube. Take care not to bend or force the expensive quartz tube.
33) Repeat this exercise with other samples. Do not position samples within one inch of the end of the heating coils that are embedded in the white furnace insulation.
34) Inspect the glass tubing adapter for a required amount of grease and dust. Wipe away dust and if there is dry glass on the ground glass surface, apply two spatula tip amounts of Apiezon grease (orange brown in color) to the surface. **Do not substitute another type of grease.** Request assistance if needed.
35) Carefully replace the greased glass tubing adapter into the female end of the quartz tube.

36) Twist the adapter ~1/8 of a turn back and forth in either direction to spread the grease over the joint surface.
37) **Temporarily** secure the glass tubing adapter in place with a green B24 keck clip. Use wire (or other inflammable equivalent) to hold the glass tubing adapter towards the quartz tube by way of the tiny glass hooks on its surface. **Remove the keck clip** when convenient. **Do not over tighten the wire**.
38) Carefully open main purge gas tank valve.
39) Carefully open the smaller, secondary purge gas valve that is found after the regulator portion of the purge gas line. Observe the oil bubbler (see photo) in order to confirm that there is sufficient flow of gas. You should observe a purge rate of approximately ~ 3-5 bubbles per second.
40) If more or less gas flow is needed, ask Dr. Rider to adjust the regulator.
41) Check the ground glass joint for shifting due to the pressure of the gas.
42) Purge the environment in the tube furnace for 20-30 min.
43) Check the ground glass joint for shifting due to the pressure of the gas.

The following instructions will run the anneal program defined according to parameters input as per the instructions above. Plan to be present for the entire ramp time and the first 5 min and the final 5 mins of the hold time of your anneal program.

44) Check that the keck clip is removed from the joint of the glass tubing adapter and quartz tube joint.
45) Remove all flammable solvents and materials from a 6 ft. perimeter around the tube furnace.
46) Place a sign near the tube furnace indicating that the unit is on and very hot. Email the research group to inform them on your runtime for the tube furnace.
47) Press and hold the downward pointing triangles ∨ to run your temperature program. You will hear a loud "CLICK" and the red run light next to the main power switch will illuminate.
48) Monitor the anneal of your samples. Observe the tube furnace during the entire ramp up time and the first 5 min of the hold condition. Inspect and make note of the tubing adapter joint, the gas tank pressure and the bubble rate in your labbook. Communicate with labmates as needed.
49) Monitor the anneal of your samples. Observe the tube furnace during the final 5 min of the hold condition.
50) Allow the tube furnace to naturally cool to less than 100°C.
51) Remove all flammable solvents and materials from a 6 ft. perimeter around the tube furnace. Once the tube furnace temperature is less than 100°C you may open the furnace lid carefully to cool the unit more rapidly. BE CAREFUL, the torsion on the tubing may want to shift the tube out of the recess in the furnace area. Monitor the

area during this final cool. Do not allow anyone to approach the area unless they area aware of the flammability risk.

52) Carefully close the furnace lid and note the unit temperature. If the system is less than 40°C, you may begin shutting off gasses, disassembly and recovering samples.
53) Turn off the purge gas by decreasing the regulator pressure (counter clockwise turns on large knob). Close the value after the regulator. Close the main tank valve. Note the final tank pressure in your lab book.
54) Handle all parts of the tube furnace and fittings with clean, grease free gloves. Contamination of the quartz tube will lead to concentrated defects in the quartz glass which will lead to thermal stress in the quartz glass and ultimately a fracture.
55) Very carefully remove any wire (or other inflammable equivalent) that might be present to keep the glass tubing adapter in the female end of the quartz tube. Take care not to bend or force the expensive quartz tube.
56) Carefully twist the glass tubing adapter to remove it from the expensive quartz tube.
57) Carefully place the glass tubing adapter on a clean kimwipe in a dust-free and secure area. Note that the tension on the black tubing will want to move the adapter after you release it.
58) Use a telescoping wand (see photo) to reach for a sample inside the tube furnace and to slide it towards the opening of the quartz tube. Take care not to bend or force the expensive quartz tube.
59) Use tweezers to carefully grab the glass (or ITO or Si) substrate. Take care to avoid dragging the sample over the greased joint surface.
60) Repeat this exercise with other samples.
61) Inspect the glass tubing adapter for a required amount of grease and dust. Wipe away dust and if there is dry glass on the ground glass surface, apply four spatula tip amounts of apeazon grease (orange brown in color) to the surface. Request assistance if needed.
62) Carefully replace the greased glass tubing adapter into the female end of the quartz tube.
63) Twist the adapter ~1/8 of a turn back and forth in either direction to spread the grease over the joint surface.
64) Temporarily secure the glass tubing adapter in place with a green B24 keck clip. Use wire (or other inflammable equivalent) to hold the glass tubing adapter towards the quartz tube by way of the tiny glass hooks on its surface. Remove the keck clip when convenient. Do not over tighten the wire.
65) Remove the sign near the tube furnace that indicates that the unit is on and very hot. Email the research group to inform them that you are finished with the tube furnace.
66) Turn the main power switch on the front of the Lindberg Blue furnace to the off position.
67) Complete the logbook with necessary information.

I. Further considerations:

c. Overview of UP150 panel:

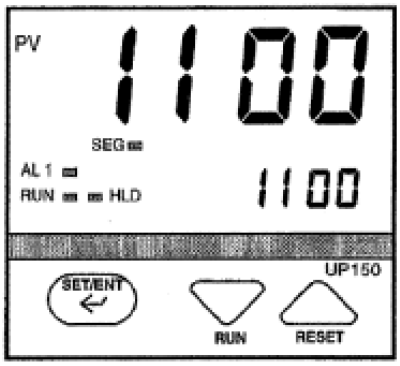


Figure 1. Image of UP150 controller

UP150 Controller Front Panel	
PV Display (red)	Process Value (chamber temperature), character information (parameter and error codes)
SP Display (green)	Target set point, parameter values

SEG lamp (green)	Lit when segment number or remaining segment time are displayed
AL1 lamp (red)	Lit when PV exceeds alarm temperature
RUN lamp (orange)	Lit when the operation mode is in RUN, flashed when operation mode is in WAIT
HLD lamp (green)	Lit when operation mode is in HOLD mode
UP key (RESET key)	Increases a parameter value, stops a running program
DOWN key (RUN key)	Decreases a parameter value, starts a program
SET/ENT key	Switches the operation display, confirms data change, switches the parameters, changes controller mode

SP1 SP 1	Target setpoint 1	Set to first target temperature
TM1 tn 1	Segment time 1	Set to desired time to allow furnace to reach first temperature (ramp) Format is "hrs.min"
SPn	Target setpoint n	Set to temperature of next segment (either hold at one temperature, or ramp to another temperature) (maximum n = 16)
TMn	Segment time n	Set to desired time for holding at a temperature or for ramp to next temperature If n is the number of the last process step, set TM(n+1) to "off" by pressing DOWN key (maximum n = 16)
JC JC	Junction code	0: Reset (default) 1: Hold 2: Repeat (repeats endlessly)
WTZ WtZ	Wait zone	Leave value at "off"

FUME HOODS

1. Process

The fume hoods are used for the handling of smelly, toxic, mutagenic or carcinogenic volatile compounds, including solids, liquids and gases. The continuous air flow is intended to prevent the accumulation of hazardous vapors and the exposure of workers to such vapors.

2. Personal Protective Equipment

Operators should wear goggles, at a minimum. Additional personal protective equipment should be used if appropriate to the hazard level of the procedure. For example, workers using acidic or caustic solutions should wear an appropriate acid/base-resistant apron and gloves. Workers using hazardous organic solvents should wear gloves resistant to that organic solvent.

3. Engineering/Ventilation Controls

The operator should confirm that there is air flow by observing a flow indicator such as a strip of magnetic tape attached to the bottom of the sash. If air is not flowing through the hood, do not use the hood, call WWU facilities to request repairs. The sash or velocity screen should be kept below the level indicated by a sticker to the side of the sash, except when absolutely necessary (e.g. when bringing oversize objects into the fume hood).

4. Handling Procedures

Avoid placing equipment or chemicals close to the front edge of the hood (this can not be avoided in the case of very large equipment).

Keep the sash glass clean. Do not obstruct your view with paper, notices, decals, or other items in the sashes.

Avoid sudden movements while working at the hood. Walking briskly past the hood can disrupt air currents and pull vapors out of the hood. Keep your head outside of the fume hood, but set equipment and perform tasks as far back in the hood as possible.

Before every use, check that there is air flow by observing a flow indicator. The sash should be operated at the lowest possible position, but not more than 18 inches.

When possible, avoid using flammable liquids in the same fume hood as a spark source such as a magnetic stirrer, hot plate, bunsen burner, or any electrical/electronic device.

5. Accident Procedures

If air flow has ceased, quickly close the sash and IMMEDIATELY call Facilities Services Emergency to arrange for repairs. Handle a fire in the hood as you would any other fire; attempt to extinguish a small fire only if others know you are doing so and if your escape route is not threatened. Be aware, however, that the air flow in the fume hood will fan the flames and may cause the fire to spread more quickly.

If there is a spill of flammable material in the hood, keep all spark sources away. Keep lab door and windows closed; the fumehood will exhaust the room and keep it at negative pressure with respect to the hall and other rooms. Call WWU's emergency line

to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.

6. Decontamination

The fume hood may need to be emptied and cleaned prior to some maintenance activities.

7. Maintenance:

- Every 6 months, wash the sash windows.
- The fume hoods are inspected by facilities and the face velocity is measured and certified to be ~100-150 fpm every 12 months. Notify facilities if the last certification was more than 12 months ago.

ULTRA-SONICATOR

1. Process

The sonicator is used for the dispersion of micro and nanostructures from samples or glassware. It can be used as a cleaning step or as a preparative step for a solution.

2. Handling Procedures

Ensure proper filling level with water. Turn on the sonicator and insert the container that contains the sample while holding it with two fingers. Depending on the intensity of the ultrasonic waves, the glass container get hot for very brief periods of time. When the colloid is dispersed remove the sample from the bath, and close the lid of the sonicator to avoid evaporation of the water.

3. Precautions

Do not sonicate fragile equipment, such as microelectrode arrays, and UV/vis quartz cells. They will break immediately!

4. Hygiene

Keep the water bath clean. Exchange water with fresh de-ionized water if necessary.

GLASS SLIDE / SUBSTRATE CUTTING & CLEANING

Being consistent and rigorous in your substrate cleaning can save you from having to repeat many experiments. Please do not cut corners here.

Supplies (adapted from Kyle Mikkelsen)

There are some supplies that you will need to prepare your substrate. For these instructions, an ITO slide will be used, but silicon wafer or passivated wafer can also be used in place. Make sure to wear gloves whenever handling any samples so they don't get contaminated by skin oils that are hard to remove. Other supplies needed include:

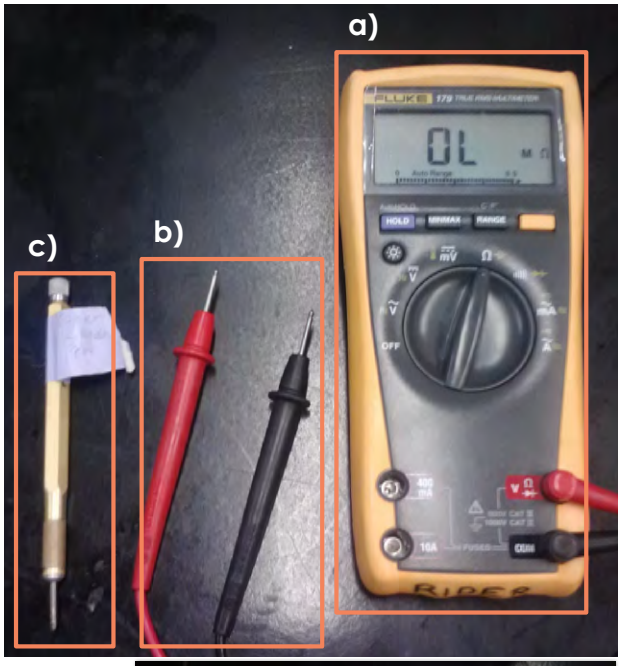
a) Voltmeter. Any kind can be used as long as it has a resistance setting (Ω symbol indicates resistance measurement as it is shown to be on in the photo)

Note: Do not leave the volt meter on while not in use, the batteries drain relatively quickly in resistance mode.

b) Voltmeter leads. These are what you use to make the resistance measurement.

c) Carbide tipped pen. This is an scoring tool used to label the substrate.

Note: The labels for a substrate should not be near the working area. For transparent substrates, it should be done backwards on the back of the slide. More detail will be given on this later.



d) This is the glass cutter. It looks like it may be upside down, but the Rider label needs to point away from you such that you have a ruler for measurements. An ITO slide is shown toward the bottom right of the photo. It may come in a plastic sleeve. Remember to use gloves.

Process

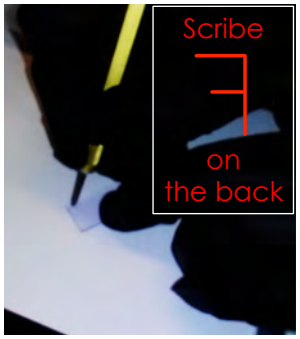
1. **Slide preparation.** After removing the slide from the packaging, you need to determine which side has the ITO. Since the ITO is conductive, the resistance measurement can tell you which side it is on. The photo at left shows a measurement of the back side where there is no ITO. This gives a zero reading on the voltmeter. The picture at right shows a measurement of the ITO side of the slide. This gives a resistance measurement, but it may vary between samples and readings. All it need to have is a reading above zero.

2. **Slide alignment.** The slide should be oriented in the cutter in the corner with the ruler along it and to the right as shown in

this side view (top photo). The red dot on the raised white brace for the silver cutter guides indicates where the carbide wheel will roll during the scoring process. You can move the white polyethylene plate to align your slide for its score mark.

3. **Slide scoring.** *The purpose of the slide cutter isn't to actually cut through the slide, but to make a score on the surface such that the slide will break along the line. The ITO side is always the one that is scored, never the bottom.* Begin with the slider far from your slide. Gently depress the button on top of the slider and move the slider towards your glass slide. At this point the carbide scoring wheel is rolling on the white polyethylene plate. Eventually the slider will stop moving indicating that the carbide wheel is at the edge of your slide. Release the button enough so that you can move the slider and wheel further and overtop of your slide, ideally such that the wheel is approximately 1/8" (2-3 mm) from the edge of your slide. Depress the slider button again to begin scoring the surface of the slide (photo at right). After pressing down you slide the cutter across the slide (usually toward you) until it stops. The amount of pressure required isn't very much and will take a little practice to get right. If you apply too much, the surface may splinter and give a bad break as shown in a few slides. If not enough is applied, the slide won't break easily leading to a bad break as well. A good cut is shown next to a poor one in a couple slides.

4. **Slide breaking.** A scored slide is shown on the right. The line is hard to see, but is shown between the two arrows. It will not score the entire surface since the cutter can't make it to the end, but it will break well anyways. To break the slide, place the scored line over a sharp edge such as the metal part of the slide cutter. Apply even pressure on the left and the right of the score to ensure an even break. Then apply even pressure to the right side until it snaps. At this point, the slide may have flipped so it is necessary to test it with the voltmeter again to ensure you know which side is the ITO.



5. **Slide labeling.** Flipping a cut slide over such that the ITO is facing down (make sure to do this on a clean surface free from dust and debris. A new kimwipe is ideal). Using the carbide pen, you can scribe a reverse letter or number on the back so that when you flip it over it looks normal through the glass. We typically etch a backwards F for face or front so that you will always know which side is the front.

6. **Slide cleaning/sonicating.** To clean the slides, separate ten minute sonications are required in three solvents in order to give a total of 30 minutes of sonication time. IN ORDER, they are dischloromethane (DCM), nanopure (NP) water and isopropyl alcohol (IPA). Try not to grab the slide with anything but tweezers at corners during and after cleaning to ensure cleanliness. Your samples are placed face-up in a clean, dust free beaker (inspect before use) that is clamped into the sonicator. With the beaker in place, make sure that the water inside the sonicator bath is at the operating level (if more is require, use fresh de-ionized water). The water needs to be at this line with the beaker submerged. You want to use enough solvent to cover all your slides being cleaned and then about 1 cm above that. Then submerge the beaker such that the solution inside the beaker and in the sonicator are approximately level with each other.

7. **Slide cleaning/sonicating cont.** After the sonicator is ready to go, make sure that the display is on. You may have to press the power button or there is a switch on the back that should typically be left on. If that doesn't work, check the power cable to make sure it is plugged in. Once on, press the degas button which is preset to sonicate for ten minutes. After sonication with one solvent, pour out the solvent into the appropriate waste container and the fill with the next solvent. Do not allow the slides to dry between cleaning solvents (this will precipitate residues on to the surface).

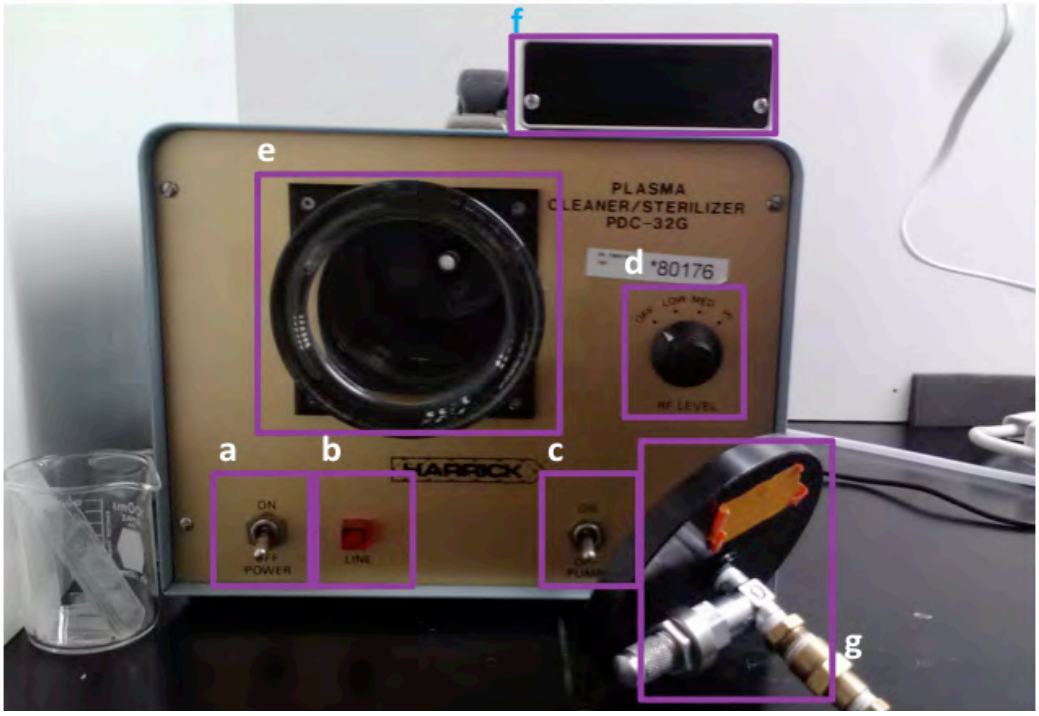
8. **Slide transport / storage.** Your slides should be dried from the final solvent (IPA) using a dust filtered air line and then plasma etched for ten minutes as per instructions in another tutorial. Use clean, dust free containers for their transport and storage (*caution*, many plastic containers dissolve in organic solvents so wet slides will be solvent-welder to their surfaces). Try not to grab the slide with anything but tweezers at corners during and after cleaning to ensure cleanliness. When grabbing slides with the tweezers, only grab them from the corner with the F on it to ensure that the ITO is uncompromised over most of the slide. The sonicator should be left with the lid on and do not turn it off.

PLASMA ETCHER

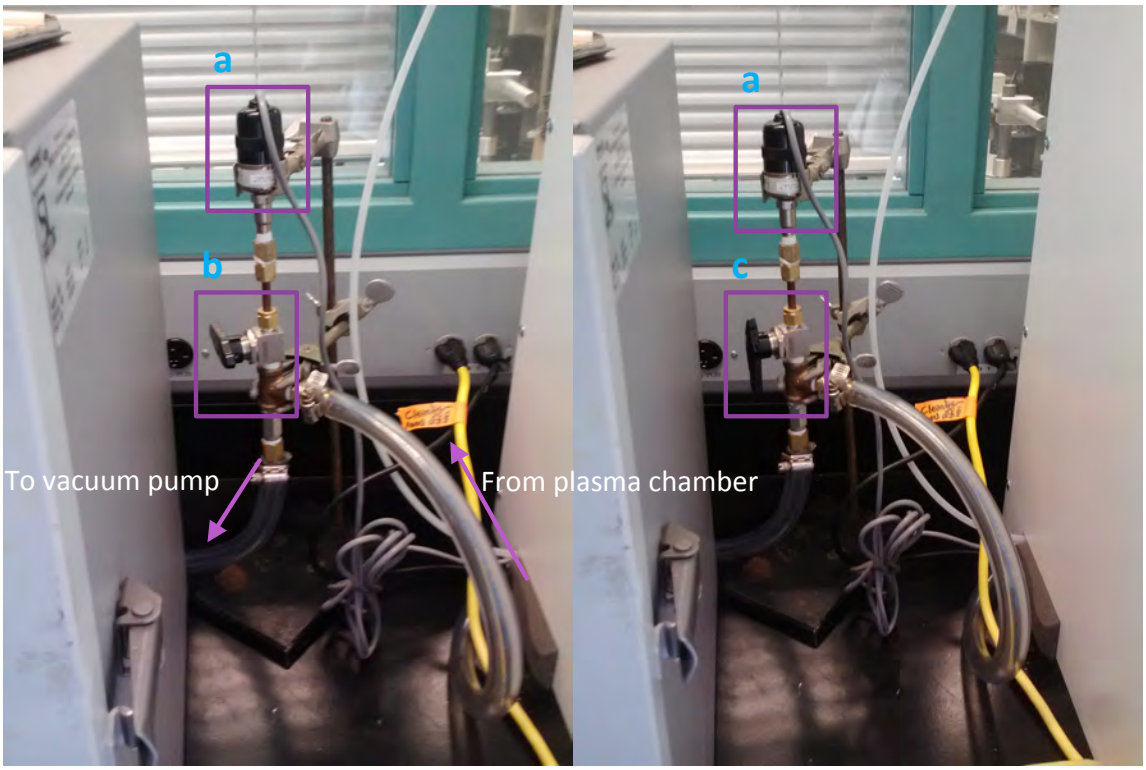
The plasma etcher is one of the most important pieces of equipment in the Rider group. If you have not received training by Prof. Rider (or someone that he has approved) then do not attempt to use the instrument.

1. Process. The plasma etcher is commonly used for the reactive ion etch of organic layers from non-metal surfaces. The organic layers should be thinner than 1000 nm. Metal ions present on the surface are typically reduced to their zero oxidation state.

2. Layout of Plasma Etcher (adapted from Kyle Mikkelsen)



a) Plasma etcher power switch. You should turn this on right away since the etcher takes a few seconds to power up before use.
b) Power light. Should come on once the power switch is turned on.
c) Pump power switch. This is not hooked up so this switch does nothing.
d) RF level. This is the power of the radio frequency on the chamber coil. We typically etch on the high setting. This is effectively the plasma "on" switch.
e) Plasma chamber. Approximately 7 cm wide and 18 cm deep glass tube where the sample is placed for etching. Microscope slides can be used stages in this space.
f) Digital pressure display. This indirectly reports the pressure in of the etch chamber. The pressure sensor is located and behind the plasma chamber and is protected from reactive ions with a manual ball valve.
g) Plasma Chamber face-plate. This door consisting of black plate with an o-ring and is vacuum sealed to the front of the plasma chamber. The silver valve is a needle valve used to control the flow of the attached gas line (argon only). This o-ring should never be touched to avoid contaminants that would compromise the seal. Dust free wipes can be used to remove contaminants if found.

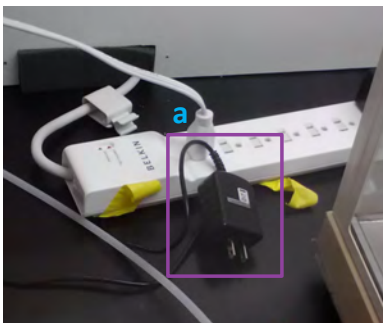


a) Pressure sensor
b-c) Valve. This valve protects the pressure sensor from the plasma since it is reactive and could ruin the plasma. The valve is closed in b and open in c.

(above) Plasma etch while running.

Since the pressure sensor is blocked off from the chamber during etching, the pressure readout will be inaccurate as to the pressure inside the chamber. As you can see, the plate is held on by vacuum and the power switches are on.

3. Handling Procedures



1. The operation is relatively simple. First, plug in the pressure sensor power chord shown in (a) at right (This is typically left unplugged when not in use). Then, open the pressure valve so that the pressure sensor can read the pressure in the line and make sure your gas tank (argon) is opened.

2. Then load your samples into the plasma etcher chamber. There are typically microscope slides left near the etcher to set your samples on so that you do not have to touch them very much shown in (b) at right.

3. While holding the plate to the front of the plasma chamber, the vacuum pump must be turned on. There are two switches for the vacuum pump. If someone is using the vacuum oven pump, then be sure not to turn it off. You may have to check both switches to make sure your pump comes on. Once it does, the plate should be suctioned to the chamber and you can let go.

4. The chamber must pump down to below 0.200. After this it must be purged with argon (or whatever gas you use). To do this, open the valve until the pressure goes up to around 3 or 4, then close the valve and let it pump back down. Repeat 2 – 3 times to ensure there is no more air left in the chamber. After this is done and the chamber has pumped back down, you are ready to get the plasma going.

5. The valve is very touchy for this portion and will require some practice. Barely crack the valve to allow some argon in. There needs to be enough argon so that the pressure is above the lowest pump-down point (which is around 0.100), but below 0.300. An ideal spot is near 0.200 but anywhere in between is allowable.

6. After the pressure is stabilized (not going up or down very much), then the pressure gauge protection valve must be closed and the plasma turned on. A cleaning step usually requires 10 minutes of etching and a polymer layer removal and metal reduction step may take longer depending on the thickness.

7. To remove samples when finished, turn off the plasma and then the pump. Open the pressure gauge valve and open the gas bleed valve to refill the chamber while supporting the chamber door with one hand. Do not force the door open. Once the pressure in the chamber equalizes with that outside the chamber the door with fall into your hand. Close the gas bleed valve on the door and close the main value on the gas tank (argon). Remove your samples making sure to not touch the surfaces that you have not etched (sample corners or glass slides as a stage is best).

8. Make sure the pressure gauge is off (unplugged) and the main power swtich to the unit is turned off. Double check that the main valve on the argon tank is closed and that the gas bleed valve on the door is closed. The face-plate can just sit on the bench in front of the chamber.

SOLVENT CABINETS BELOW FUME HOODS

1. Process

The solvent cabinet is used for the storage of flammable and combustible organic liquids.

2. Engineering/Ventilation Controls

The flammables cabinet has self-closing doors.

3. Handling Procedures

The cabinet should not be used to store more than 227 litres (60 US gallons) of flammable liquids. Up to 38 litres (10 US gallons) can be outside the cabinet at any one time. The cabinet doors must be kept closed except when removing or replacing a bottle. Do not use any device to prop open the doors.

4. Accident Procedures

If there is a fire in the flammables cabinet, evacuate the room and the building immediately and call WWU's emergency line. The cabinet doors should close on their own.

If there is a spill in the flammables cabinet, keep all spark sources away. Keep lab door and windows closed; the fumehood will exhaust the room and keep it at negative pressure with respect to the hall and other rooms. Call WWU's emergency line to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.

5. Decontamination

The solvent cabinet may need to be cleaned prior to repair or disposal. If organic residues are visible, these should be scraped or washed off and added to a properly labeled hazardous waste container. If no residues are visible, wipe the surfaces with wet paper towels.

6. Maintenance:

If the doors fail to close at any time, adjust the feet of the cabinet, oil the doors, or request repair assistance from the machinist or the manufacturer.

REFRIGERATOR/FREEZER

1. Process

The refrigerator/freezer is used for the storage of chemicals. The electrical components and switches are isolated from the internal atmosphere to prevent the possibility of a spark-induced fire.

2. Hazardous Chemicals

The refrigerator may contain a wide variety of hazardous chemicals, including flammable, reactive or toxic compounds. Under no circumstances should food or drink be stored in this fridge.

3. Personal Protective Equipment

Operators should wear goggles, at a minimum. Workers using hazardous organic solvents should wear gloves resistant to that organic solvent.

4. Handling Procedures

The refrigerator/freezer doors must be kept closed except when removing or replacing a bottle. Open the door slowly to prevent agitation of chemicals containers stored in the door shelves.

5. Accident Procedures

If there is a fire in the refrigerator/freezer, evacuate the room and the building immediately and call WWU's emergency line.

If there is a significant spill of a flammable material in the refrigerator/freezer, keep all spark sources away. Keep lab doors and windows closed; the fumehood will exhaust the room and keep its pressure negative with respect to the hall and other rooms. Call WWU's emergency line to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.

6. Decontamination

If necessary for decontamination, remove the freezer door and pivot down the evaporator assembly to obtain complete access to the cabinet interior.

9. Maintenance:

Wipe clean the wire shelves periodically. Clean the inside surface of the cabinet with warm water with detergent. Rinse thoroughly with clean warm water and wipe dry. Be sure the power is off before cleaning.

Defrost the freezer as required.

Every 6 months, clean the condenser coils with a soft brush or a vacuum cleaner with a brush attachment. Be sure the power is off before cleaning.

Do not modify or work on any electrical components. Contact WWU's facilities Service for any repairs.

GAS/VACUUM MANIFOLD

1. Process

The gas/vacuum manifold is used for the handling of air or water sensitive chemicals. It consists of a gas manifold (for delivering either argon or nitrogen), a vacuum manifold (for evacuating glassware), and a vacuum pump (attached to the vacuum manifold). The inert gas is supplied by a gas cylinder via a regulator, passes through the gas manifold, and then bubbles through an optional oil bubbler.

2. Hazardous Chemicals

The gas/vacuum manifold is used for the handling of air or water sensitive chemicals. Some of these chemicals could be very pyrophoric. Other than the hazards of the chemicals to be handled, the principle hazards of the gas/vacuum manifold include explosion due to overpressurization, implosion of evacuated vessels, frostbite from contact with liquid nitrogen, and overheating during regeneration of the drying catalyst. The inert gas, argon, if vented in sufficient quantities, could displace enough air to cause asphyxiation of people in the room. However, standard size argon gas cylinders contain only 330 cu. ft. or less of gas while room 203 contains approximately 12,000 cu. ft. of air.

Oil bubblers are used at the exit of the gas manifold. Mercury should not be touched and its vapors should not be inhaled.

3. Personal Protective Equipment

Operators should wear goggles, at a minimum. Workers using mercury or hazardous organic liquids should wear gloves resistant to those materials.

4. Engineering/Ventilation Controls

The oil or mercury bubbler serves to allow inert gas to escape from the manifold if the pressure rises over 1 atm. The bubbler also prevents air from coming into the manifold The mercury bubbler must always be held in or over a bucket, and the vent from the bubbler must be directed into the same bucket or a different bucket. Thus mercury spills should be contained. The mercury bubbler has an extra bubbler before it and another after, to catch any mercury sucked back or blown out of the main bubbler.

5. Handling Procedures

Replacing a gas cylinder: Close the fine valve on the regulator and the valve on the old (empty) cylinder. Detach the regulator from the old cylinder. Put the cap on the old cylinder. Unstrap and remove the old cylinder and put in its place the new argon or high-purity nitrogen (99.97%) cylinder. **Do not move a cylinder unless its protective cap is in place.** Strap in the new cylinder and remove its the cap. Attach the regulator and open the cylinder valve but not the fine valve. Close the cylinder valve again and open the joint between the cylinder and the regulator slightly to let the pressure escape. This allows the connection to be flushed with gas. Then tightly attach the regulator, and slowly open the regulator valve.

When starting to use the vacuum manifold, confirm that all of the valves leading to the flexible tubing are closed, check that the trap bottoms are attached to the trap, and then put liquid nitrogen into two Dewar flasks and put them around the traps. Turn on the

vacuum pump. *When finished* with the equipment, reverse the above procedure. That is, turn off the vacuum pump, open the valves which allow air into the traps, and remove the liquid nitrogen Dewar flasks from around the traps.

WARNING NOTE: After you remove the liquid nitrogen Dewar flasks, if you see a clear blue (oxygen) liquid in the traps, Close the sash of the fume hood and **LEAVE IMMEDIATELY**. Do not continue with the procedure, because the oxygen may explosively react with organics in the trap. After about 10 minutes, the liquid will have boiled off and passed through the pump. If the liquid was oxygen, this will have created a temporary fire hazard (hence the need to leave the room).

Evacuating a flask: Examine the flask for cracks before evacuating it. This will reduce the risk of implosion. Always secure evacuated flasks, so that they cannot fall or roll on the benchtop, and explode.

Beware of condensing argon. Argon's boiling point (-185.7°C) is higher than that of nitrogen (-195.8°C). It is therefore possible to condense liquid argon. If a vessel containing condensed liquid argon were closed and then removed from the liquid nitrogen coolant, the vessel would explode.

Beware of condensing oxygen. Oxygen's boiling point (-183.0°C) is higher than that of nitrogen (-195.8°C). It is therefore possible to condense liquid oxygen. If a vessel containing condensed liquid oxygen were closed and then removed from the liquid nitrogen coolant, the vessel would explode. Also, if liquid oxygen condensed in a vessel or trap along with some flammable or combustible compounds, an explosive reaction could result.

Degassing a liquid. Choose a round bottom Schlenk flask of the appropriate volume. Evacuate the flask and then fill it with argon or nitrogen. Add the liquid by syringe or pipette. Close the sidearm stopcock and cool the flask in a dewar with liquid nitrogen until the liquid freezes. Then evacuate the vapor phase by turning to vacuum and opening the sidearm stopcock. After 1 minute, start thawing the vessel. When some melting of the solid is observed, turn the stopcock to argon/nitrogen. Keep the sidearm stopcock open. When the solid is completely melted (but not necessarily warmed to room temperature) repeat the procedure. A total of three cycles is usually sufficient.

6. Accident Procedures

If there is a large fire, evacuate the room and the building immediately and call WWU's emergency line.

If there is a significant spill of a flammable material, keep all spark sources away. Keep lab doors and windows closed; the fumehood will exhaust the room and keep its pressure negative with respect to the hall and other rooms. Call WWU's emergency line to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.

If there is an implosion or explosion due to vacuum or overpressurization and no subsequent fire, close off the valves leading to any vessels containing chemicals, remove the liquid nitrogen dewars, turn off the vacuum pump, allow air into the traps, and turn off the argon supply.

After you remove the liquid nitrogen Dewar flasks, if you see a clear colourless (argon) or clear blue (oxygen) liquid in the traps, **LEAVE IMMEDIATELY**. Do not

continue with the procedure, because the oxygen may explosively react with organics in the trap or it may boil so quickly that the glassware bursts. After about 10 minutes, the liquid will have boiled off. If the liquid was oxygen, this will have created a temporary fire hazard (hence the need to leave the room) and will have made it necessary for the oil in the pump to be replaced.

7. Waste Disposal

Waste argon gas can be vented. Liquid wastes condensed in the traps should be disposed of in a manner appropriate to their nature. Organic condensates can be poured into a properly labeled organic hazardous waste container. Waste mercury should be labeled as hazardous waste and sent for disposal separately from other hazardous wastes.

Spent catalyst is pyrophoric; it should be wetted prior to its discharge and stored and transported in a wet condition.

8. Approval Required

No prior approval is required for use of the gas/vacuum manifold, but use of the equipment is restricted to those people who have been trained in its use by a competent user and who have read these SOP's and signed on their training form that they have read these SOP's.

9. Maintenance:

The pump should be serviced as described in its manufacturer's manual.

BASE BATHS

1. Process

The base bath is used to clean glassware.

2. Hazardous Chemicals

The base bath contains isopropanol and potassium hydroxide. Isopropanol is flammable. Potassium hydroxide solutions are caustic. Do not inhale the vapors from the bath.

3. Personal Protective Equipment

Operators must wear goggles and isopropanol- resistant gloves with medium or long sleeves. A lab coat and splash apron is also required. Do not put your unprotected hand in either bath. The base bath is not only caustic but it is organic, so your skin offers no protection from any toxic impurities in the bath.

4. Engineering/Ventilation Controls

Always keep the bath tightly covered except when transferring items. Keep spark sources away from the base bath.

5. Handling Procedures

To prepare the base bath, dissolve 500 g KOH in 1.5 L of distilled water. After the KOH dissolves, add 8 L of isopropanol. To prepare the acid bath, add 0.5 L HCl to 8 L of distilled water.

To wash glassware in the baths: Hand wash the glassware with soap and water. Rinse off the glassware with distilled water thoroughly and shake off excess water before putting it into the KOH/^{i}PrOH bath. Leave it in that bath for at least an hour. Remove it from the bath, let excess ^{i}PrOH drip back into the bath. Rinse off the glassware with distilled water before putting it into the dilute HCl bath. Leave it in that bath for at least 30 minutes. Remove it from the bath, let excess HCl drip back into the bath, then rinse again several times with distilled water and let it dry.

Do NOT put any of the following items into the KOH/ ^{i}PrOH bath:

- excessively dirty glassware. All surfaces should be > 95% transparent. Any visible solid and liquid contaminants in the glassware should be removed first.
- volumetric glassware
- stopcock keys
- glass frits/filters
- rubber items
- IR or UV cells or NMR tubes
- fragile or broken glassware
- glassware that still has grease or bulk dirt on it
- anything with mercury, sodium, potassium metal
- anything with high acute toxicity (e.g. mercury, thallium or cyanide salts)

To wash NMR tubes, don't put them in the baths. Rinse the empty NMR tubes with acetone, then dilute HCl, then distilled water, then acetone. If the tubes are still dirty, rinse them with distilled water then fill them with KOH/ ^{i}PrOH from the bath, leave them for an hour in the fume hood (no longer than 1 h), then dump the contents back into the bath. Rinse with distilled water then repeat with the dilute HCl. Rinse and dry. If elemental metal solid remains on the NMR tube, fill it with aqua regia (3:1 HCl:HNO_3) and leave it overnight in the fume hood. Then rinse with distilled water and repeat the KOH/ ^{i}PrOH and HCl treatments.

To wash UV cells, don't put them in the baths. Hand wash with soap and water. Rinse off with distilled water thoroughly and shake off excess water before rinsing them with acetone, and air dry them.

6. Accident Procedures

If there is a fire, evacuate the room, closing the door behind you. Pull the fire alarm and call 911.

If there is a spill of the base bath, keep all spark sources away. Keep lab doors and windows closed; the fumehood will exhaust the room and keep its pressure negative with respect to the hall and other rooms. Call 911 to report the incident. The Hazardous Materials Emergency Response Team will supervise the cleanup.

7. Waste Disposal

After deactivation (see Handling Procedures), the aqueous phases may be packaged as hazardous waste for disposal.

8. Maintenance:

Always keep the baths covered. If evaporation occurs, top up with ^{i}PrOH for the base bath or distilled water for the acid bath.

WASTE DISPOSAL

Respect the waste disposal training as described in your lab researcher training session.
Heavy metals (especially Hg) must be prepared separately for disposal.

Organic Waste
Separate halogenated from non-halogenated chemicals.
Keep the cap on **but leave it loose** to vent in case of inadvertent reaction in the container. Do not leave funnels in open containers.
- Don't put any waste in the bottle until the bottle is properly labeled with a hazardous waste label.
- Experimental procedures involving reactive species (eg. acids, bases, oxidizers, reducers, metal alkyls, hydrides) should include a neutralization as the last step in the procedure. Never put reactive species into the waste before such a neutralization step, or they may react with the other components already in the waste.
- No inorganic solids, precious metals, or mercury may be put in the organic waste.
- Leave ~1/4 bottle of headspace in the bottle.

Other types of Waste
- Keep mercury waste in a separate container, properly labeled as hazardous waste.
- Unused silica gel, alumina, celite: put in a ziploc and then in the garbage.
- Used silica gel, alumina, celite should be put in a solid waste container.

Disposal
- Dispose of wastes **promptly**, preferably within 3 months from the start of waste accumulation in that container. No waste should be accumulated beyond 9 months.

Selected Instruments

Glovebox Spincoater (Laurell WS-400-6NPP-Lite):

Updated 05/03/2017 by Dr. Rider

Before you begin…

1) Ensure that you can safely program and operate the spincoater in the dust-free hood before attempting any glovebox spincoating.
2) Ensure that you have been properly trained on glovebox use and know how to correctly execute an atmosphere purge procedure.
3) Consult with fellow group members on their need to use the glovebox and the neighboring RRDE electrochemistry setup. The spincoater shares a N2 tank with the RRDE and therefore both cannot be operated at the same time.

Part A: What to bring into glovebox

1) A precut new Al foil liner for the spincoater. You can size/shape this at the spincoater in the dust-free hood.
2) Cleaned and dried substrates in a holding dish. Use plastic petri dishes with caution as trace solvents from the spincoat will "solvent weld" substrates to the dish.
3) Spincoating solution (unless already prepared in glovebox)
4) Syringes and needles with needle cap. Syringe filters if needed.

Part B: Turning on N2 gas and Vacuum Pump for Spincoater

1) Locate the spincoater nitrogen tank. Shift the spincoater so that you will be able to read its LCD display while making adjustments at the spincoater nitrogen tank.
2) Flick the switch on the vacuum pump beneath the glovebox to the on position (a small white dry-sec pump). The vacuum provides negative pressure to the chuck in the spincoater to hold your substrate in place. The vacuum will also draw atmospheric pressure from the glovebox if the seal with a substrate is poor. Do not leave the glovebox unsupervised with this vacuum running.
3) Open the green valve connected to the pump's line that runs to the glovebox and spincoater.
4) Ensure that the large regulator dial on the spincoater nitrogen tank has been turned all the way out (counter-clockwise) so as to not provide pressure to either of the lines.
5) Note the position of the three-way valve on the output of the regulator on this tank. It should be in the off position (the pointed end of the value pointed midway between the two output lines). Turn it such that the pointed end aligns with the line feeding N2 to the spincoater (a segment of black PE tubing).

6) Observe the spincoater LCD, you should see a flashing "CDA" in the top right. **Slowly** adjust the large regulator dial (clockwise) so as to increase the pressure output from the tank. Building this pressure all the way to the spincoater will eventually cancel the "CDA" warning signal indicating there is now sufficient pressure to drive the spinning of the substrate chuck. Usually ~50-55 psi is required on the output of the regulator for this.

7) Note: the spincoater now is feeding additional N2 to the glovebox. The glovebox will vent any excess pressure from this feed using its pressure relief solenoid valve. You will hear this valve open more often, once ever 5 secs or so. Try to minimize the time that the spincoater is in this state to avoid over-burdening the glovebox pressure regulation system.

8) Place your new Al foil liner into place in the spincoater cavity. You will discard this after your spincoating session.

9) Turn off the circulator blower for the glovebox catalyst.

10) Close the Valves for the glovebox catalyst.

11) The spincoater can now be used as per normal.

12) Close all solvent and solution containers.

13) Gather up your waste and your Al foil from the spincoater. Place all solvent contaminated waste in the antechamber.

14) Dial down the regulator on N2 tank feeding the spincoater (counter-clockwise) until the pressure is zero, or until the dial spins freely.

15) Turn the three-way valve to the off position. The pointed end of the value should be pointed midway between the two output lines.

16) Check that the "CDA" is flashing on the LCD of the spincoater.

17) Close the green value on the vacuum pump for the spincoater.

18) Flick the switch on the vaccum pump to the off position.

19) Purge the glovebox atmosphere with 300 psi of N2.

20) Open the glovebox catalyst valves.

21) Slowly turn the circulator blower back to its on position and speed (black arrow on tape).

22) Complete the glovebox logbook with the information on the glovebox N2 tank and that for the spincoater. Note any other required details in the logbook.

TGA MS: Hiden QGA – Perkin TGA 4000

Updated 01/29/2016 by Natasha Siepser and Dr. Rider

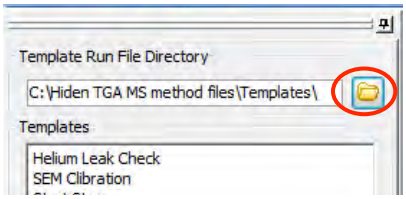
Before you begin…

1) Sign in to the TGA-MS log book.
2) Check the previous entries in the log book to confirm if the white alumina sample tube is attached to the end of the mass spectrometer capillary.
3) If the white alumina sample tube is not installed and is required for your TGA-MS experiment or if you needle the sample tube removed, consult Dr. Rider or an approved experienced user for assistance.

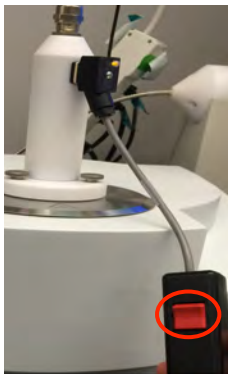
*If this is your first time using the TGA-MS please proceed to **Part A** to configure the start stop button on the Hiden MASsoft7 software. If you have already configured the start stop button to MASsoft7 software, proceed to **Part B**.*

Part A: Configure start stop button to the MAsoft7 software

1) Turn the power button on for the Hiden QGA mass spectrometer (green button located on the front panel in the bottom left-hand corner; wait for a beep before proceeding to next step)
2) Open the "MASsoft7" program window
3) In the "MASsoft7" program window, select templates (located in the bottom right corner of the screen)



4) In the Template Run File Directory, input the following location by selecting the folder icon and searching for Local Disk (C:)/Hiden TGA MS Method Files/Templates.
5) In the white box that says Helium Leak Check and SEM Calibration, right click and select refresh.
6) Select Quick Start (located in bottom right corner of screen)
7) Select the button "Click to customize."
8) In the Custom Button 1 drop down menu, select 'start stop' then press ok.
9) The start stop button should now appear on the Quick Start menu.



Part B: Setting up TGA-MS experiment

1) Turn on the power to the base of the heat coil on the capillary transfer line between the TGA and the MS (this is a red switch attached to the TGA, there should be a light illuminated)
2) Turn on the nitrogen gas tank. Do not adjust the regulator.
3) Turn on the recirculator / chiller to provide coolant to the TGA (a blue button with a circular arrow on it). The recirculator / chiller is below the table.
4) Log on to the computer.

5) Turn on the TGA 4000 by flipping a switch at the back left corner of the instrument. Wait for the "Control" light to blink.
6) Open the Pyris Manager program. A Pyris work bar at the top of the screen will appear.
7) Click the "TGA 4000 Offline" icon in this work bar. The software takes about 2 minutes to load. Be patient and do not click the icon numerous times as you wait. The icon will update its status as the software appears and as it connects to the TGA 4000.

8) In the Pyris software program go to "Tools" and then "Preferences." Make sure that the "Use Relay Box" has been checked. Do not change any other settings.

9) In the Pyris software window, mouse over to file and select either New Method (if you want to create a new method file) or Open Method (if you have an existing file that you will be using). You will populate and verify the parameters for the desired method in step 21.

NOTE: Follow step 9 even if the method you are wanting to run is already populated in the Method Editor pop up window. By selecting Open Method, the trigger box, which is responsible for communication between the TGA and mass spectrometer is reset (this is necessary for the TGA and mass spectrometer to communicate with each other).

A sample method for calcium oxalate hydrate may be found on the Local Disk (C:)/ Program Files (x86)/ Perkin Elmer/ Pyris, method/ Rider Group/ calcium oxalate hydrate.

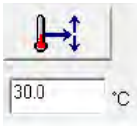
For steps on creating a new method refer to Part D.

10) Carefully unscrew the three finger screws on the Teflon transfer base located on the top of the TGA 4000. Be mindful of each of the washers that are used with each of the three finger screws. Carefully set the screws aside being sure not to lose the washers.
11) Carefully lift the Teflon transfer base away from the TGA 400 and set it aside on a clean surface (Kimwipe).
12) Use clean tweezers to carefully remove the white TGA pan (cup-shaped) from the furnace area in the TGA. There may be residual powder from a previous sample so do not spill or drop the pan.
13) Gently pour out previous sample residues into a glass beaker (the beaker will catch the pan if you drop it). You can use a spatula to tap at the tweezers to shake residue from the pan.
14) Replace the clean, empty pan into the TGA furnace area.

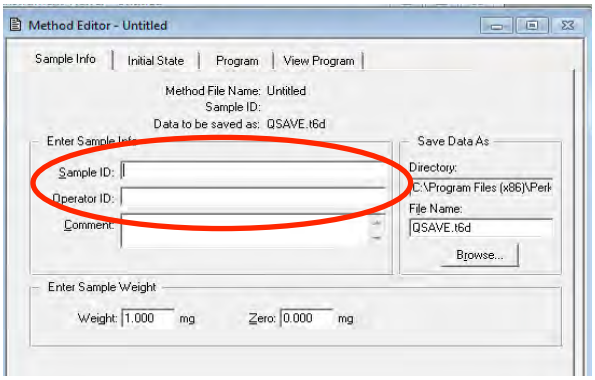
15) Replace the Teflon transfer base and finger screws (take care not to lose the washers).
16) Wait 1 min for the mass of the pan to stabilize (do not bump of shake the table at this point).

17) Click the "Zero Weight" button (looks like a level blue balance beam). Inspect the Weight and % Weight fields in the software. These should be close to zero.

18) Click the "Reset Monitor" button (looks like a grey eraser erasing a quarter of a graph).



19) Enter 30.00°C in the Temperature field above the buttons in the right control panel.
20) Click the "Go to Temperature" button that is above this field (looks like a thermometer with a vertical double arrow).



21) Select the "Sample Info Tab" in the Method Editor Window. Complete Sample ID, and operator fields. Do not change any of the mass information below.
22) Ready a clean petri dish for sample loading.
23) **Consult with Prof. Rider on the mass of sample to be analyzed**. A polymeric sample should not be run to full degradation and should not be studied with an analysis mass in excess of 0.05 mg. Samples that only degrade to highly volatile gases (i.e. water, CO_2, CO, SO_2, etc…) can be run at higher masses of ~2 mg. Samples with masses outside of these guidelines that are run on the TGA-MS will lead to a permanent blockage of the capillary transfer line ($500 and 1 week downtime for the instrument).
24) Carefully unscrew the three finger screws on Teflon transfer base located on the top of the TGA 4000. Be mindful of each of the washers that are used with each of the three finger screws. Carefully set the screws aside being sure not to lose the washers.
25) Carefully lift the Teflon transfer base away from the TGA 400 and set it aside on a clean surface (Kimwipe).
26) Use clean tweezers to carefully remove the white TGA pan (cup-shaped) from the furnace area in the TGA. Place this in the clean petri dish.
27) Transfer an appropriate mass of sample to the TGA pan (for example, Calcium Oxalate monohydrate can be studied with 1-2 mg).
28) Carefully replace the TGA pan with the sample into the TGA furnace area.
29) Replace the Teflon transfer base and finger screws (take care not to lose the washers).

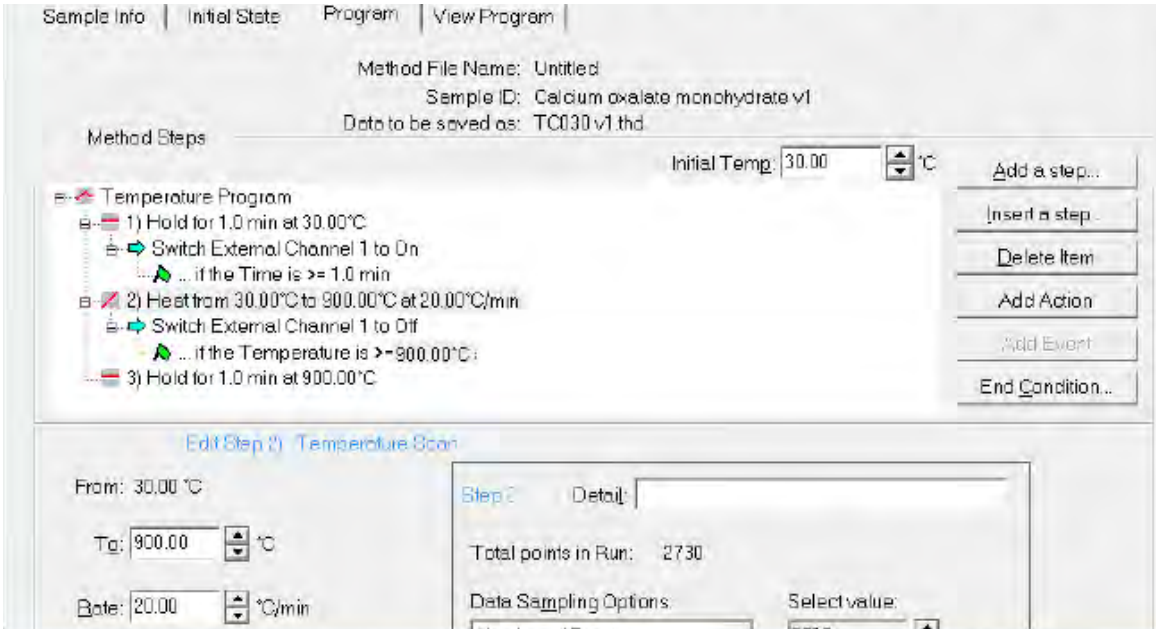
30) Wait 1 min for the mass of the pan to stabilize (do not bump of shake the table at this point).

31) Click the "Sample Weight" button (looks like a non-level balance beam). Inspect the Weight and % Weight fields in the software. The "Sample Weight" field in the "Sample Info Tab" in the Method Editor Window should now have a value close to what is observed in the Blue Weight readout.

32) Select the "Initial State" tab in the Method Editor Window. Type in 30.00°C for the initial temperature (under set initial values).

33) Select the "Program" tab in the Method Editor Window.

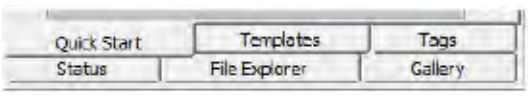
34) Use the expand buttons (looks like a "+") and "Add a Step" and/or "Add Action" buttons at right to modify the method. Modify the "To:___" and "Rate:___" fields below the method steps to define your TGA study (for a 20°C temperature ramp from 30° to 900°C the fields will be 900 and 20, respectively):



35) Inspect your temperature program. The first hold temperature should match the "Go to temperature" from earlier. The first hold temperature should also match the "initial state temperature" from earlier. The time value in the first "flag" field should match the time value in the first hold step. The temperature value in the second "flag" field should match the final temperature of the ramp. The last hold temperature should also match the final temperature of the ramp.

36) If not already done, turn the power button **on** for the Hiden QGA mass spectrometer (green button located on the front panel in the bottom left-hand corner; wait for a beep before proceeding to next step)

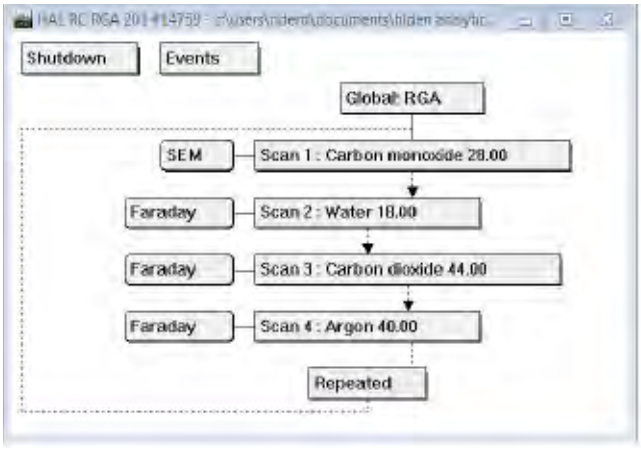
37) If not already done, mouse over and click the "MASsoft7" program window.



38) Click the "Quick Start" Tab in the bottom left area.

39) Click the "11644 Start_Stop" button. Accept any automatic request for "Views."
40) An error message may pop up saying that "This file was created on a different instrument. Convert and check the file before running." Select ok.

41) Click File then Convert File or the Convert File icon (looks like downward pointing arrow with a two grey boxes above and below it). When a pop-up window appears, click yes.



42) Double Click the "Scan 1: water 18.00" field in the "HAL RC RGA …" Window.
43) Click the "MID" tab below (bright green font) and select 18.00 AMU for water. Click ok.
44) Double Click the "Faraday" field next to Scan 1 in the "HAL RC RGA …" window. If you want to use the SEM detector you can switch to this detector at this point. For most trace volatile analytes the Faraday detector is best. Click ok.
45) In the "HAL RC RGA …" window, click "Create New Scan to be performed in Sequence." (this icon is in the upper right corner)

46) A new scan should appear in the "HAL RC RGA …" Window.
47) Double Click the "Scan 2: _____" field in the "HAL RC RGA …" Window.
48) Click the "MID" tab below (bright green font) and select the correct ____ AMU for the next analyte of interest. Click ok.
49) Double Click the "Faraday" field next to Scan 2 in the "HAL RC RGA …" Window. If you want to use the SEM detector, you can switch to this detector at this point. For most trace volatile analytes the Faraday detector is best. Click ok.
50) Repeat Steps 45-49 as needed.
51) A typical completed scan definition ("HAL R RGA …") for the volatiles release from calcium oxalate monohydrate is shown above.

52) In the "HAL RC RGA…" window, press Ctrl on the keyboard and select Scan 1, Scan 2, etc. (select all scans of the masses being analyzed) Then press the binoculars icon.

53) Push the "Execute Scan" button. Wait 1 min as the software engages.
54) Inspect the text area below the MASsoft7 tabs for a comment that reads: "Waiting for data." At this point the MS software is waiting for External Channel 1 signal from the relay box from the TGA software to allow the MS to write data.

<u>If the "Waiting for data" comment does not appear and instead the mass spec. scan goes directly into data acquisition, press the stop icon in the MASsoft 7 software. Refer to Part F:</u>

Troubleshooting.

55) Once the "Waiting for data" comment has been located. Mouse over to the Pyris TGA software.
56) Click the "Start/Stop" button in the Pyris TGA software to begin the run.
57) Once the run is complete & the temperature of the TGA furnace is < 300°C:

a. Turn off the power to the base of the heat coil on the capillary transfer line between the TGA and the MS (this is a red switch attached to the TGA, the illuminated light will go off). Cool the TGA to < 100°C by removing the Teflon transfer base and by clicking the air cool icon.
b. Save the mass spectrometer data by selecting file, save as, change the file name to something you will recognize and select a location to save to. (the mass spectrometer data will automatically save the data as file # to Local Disk (C:)/ Users/ Your Username/ My Documents/ Hiden Analytical/ MASsoft7/ Templates upon experiment completion.
c. In the Pyris sofware save the thermogram by selecting file and "save data as" in order to save the file to the desired location. (the TGA will automatically save to the Local Disk (C:)/ Program Files (x86)/ Perkin Elmer/ Pyris/ data)
d. If no data workup is to be done at this time proceed to shut down steps below, otherwise, proceed to Data Work Up procedure outlined in **Part C**.
e. Turn off the recirculator / chiller to stop the coolant from flowing to the TGA.
f. Turn off the nitrogen gas. Do not adjust the regulator.
g. Close the MASsoft 7 software.
h. Switch the green on/off switch to off on the front left of the Hiden QGA.
i. Close the Pyris TGA software.
j. Turn off the TGA 4000 with the switch at the back left of the instrument.
k. Return back to the log book and write any comments or problems encountered when using the TGA-MS. Also, indicate if the white alumina sample tube was used.

Part C: DATA Work-Up

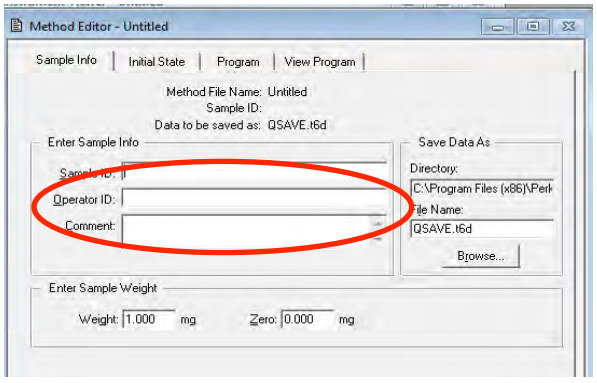
1. If not already done, make sure the green power switch on the front left of the Hiden QGA mass spectrometer is **on**.
2. Open the MASsoft7 software.
3. Open the data file of interest for data workup by selecting file, open, and selecting the file.

4. With the data view file selected, mouse over to File, Export, DDE.
5. In the DDE link selection pop up window, select data, then click Options…
6. In the MID Data pop up window, **deselect** hh:mm:ss and make sure the milliseconds (ms) box is checked. Then press ok.
7. In the DDE link selection pop up window, press ok. The window will disappear.
8. Before clicking anywhere else, press ctrl + c to copy the data.
9. Open the excel converter file found in Local (C:)/ Users/ Public/ Public Documents/ Excel 2010 TGA MS converter file/ Translate text file writer.
10. Delete any existing data in Column A and B and paste copied data from the MASsoft7 software.
11. In excel, press ctrl-t. A pop up window should appear. Save the file as a .txt (Text Document File).
12. Mouse over to the Pyris software.
13. Open the TGA data file if not already open by selecting the data analysis icon and finding the data file of interest.

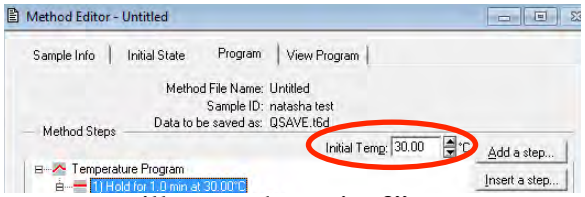
14. Select the TGA data window that the mass spectrometer data will be overlaid into. Click the "Temperature/time x-axis" icon to convert the x-axis of the thermogram from temperature to time.

15. Click File, Import Data, X-Y Data. Open the saved excel file form step 11.
16. In the imported data pop up window, select ok. In the "Generate temperature or time data for imported file" select calculate.
17. The mass spectroscopy data should now be overlaid on the TGA thermogram.
18. To change back to a temperature x-axis, click the "temperature/time x-axis" icon.
19. Save the overlaid thermogram and mass spectrometry data.

Part D: Create a new method



a) In the method editor window, sample info tab input information for sample ID and Operator ID.
b) Select the "Program" tab in the Method Editor Window.
c) The intial temperature can be adjusted by inputting a temperature.
d) Click the "Add a Step" icon and select an option and press ok.
e) Click the "Add Action" icon and select "trigger an external event". From the drop down menu, select "switch external channel 1 on On" and press ok. In the "What event will cause the action?"



window select “a specified time is reached” and select ok. In the “Time Event” pop up window, adjust time to desired length and press okay.

f) More steps for the method may be added by clicking “Add a step” and selecting an option and pressing ok.

Part E: MASsoft 7 Gas Calibration

i. Set up a gas tank containing a known mixture of gases next to the TGA MS.

ii. Set up an airtight empty flask and rubber septa configuration. Purge the flask’s headspace with the gas mixture of interest. Attach a needle through the septa that runs to a bubbler to prevent pressure build up. Allow the gas mixture to purge the system for several minutes before proceeding to the next step.

iii. Set up an MID experiment in the MASsoft 7 software to analyze the gases present.

iv. Attach a needle and tubing to the capillary tube and insert the needle through the septa.

v. Start the MID experiment in the MASsoft7 software.

vi. Allow the MID experiment to run until each gases’ partial pressure is no longer changing.

vii. Press the stop icon.

viii. Use the gas calibration file to determine the relative sensitivity. The calibration file is located Local Disk (C:)/ Hiden TGA MS method files, MASsoft Calibration/ Calculating Relative Sensitivity for Three Gasses.

ix. After calculating the relative sensitivity, mouse over to the “HAL RC RGA…” window in the MASsoft 7 program.

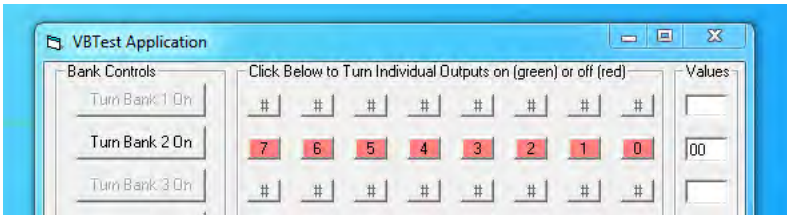
x. Click on gas scan # that corresponds to the gas that was just analyzed for its relative sensitivity.

xi. In the pop up window “scan editor”, press the unlock icon, and enter the value into the relative sensitivity field.

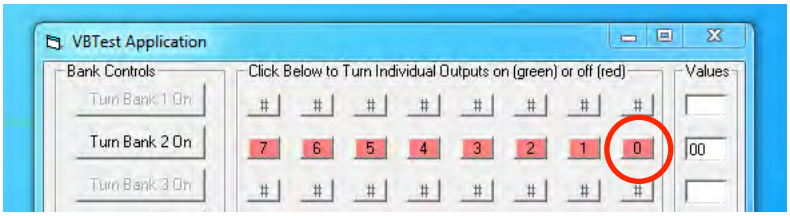
Part F:Troubleshooting

A) Follow the steps below if the mass spectrometer does not go into “Wait for data” mode, but instead starts data acquisition immediately in Part B step 54.

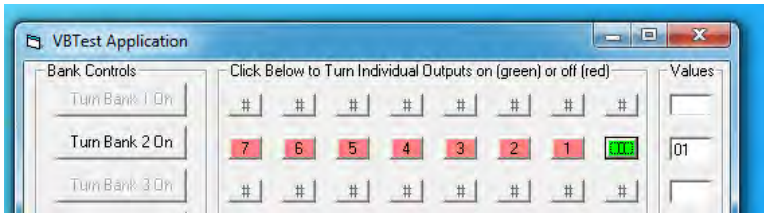
i. Go to Start, All Programs, Seal I0, VB_test application. You should see the below window.



ii. Press the top right red box with the red circle around it once to turn the serial box on.



The window should now look like the picture below.



iii. Press the top right green box once to turn off the serial box. The box should turn red. You have now reset the serial box.

iv. Return the MASsoft 7 program and proceed with Part B: step 53.